

ANISOTROPY OF EPR SPECTRUM OF SYSTEMS DESCRIBED BY
A MONOCLINIC SPIN HAMILTONIAN WITH $S = 1$ *

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(Received May 17, 1971)

The angular dependence of resonance field for a system described by a monoclinic spin Hamiltonian with $S = 1$ is calculated in the second order of perturbation procedures for strong and weak magnetic fields. The low symmetry effects are found to consist in:

departure from 90° -distance between the angles of extremal resonance field values in the plane perpendicular to the two-fold symmetry axis,

angular asymmetry according to the directions of the above extremal values,

non-coincidence of extremal field directions for different transitions,

occurrence of more than two extrema within a 180° -period,

deviations from 180° symmetry of the spectrum.

The secular equation is solved for approximate directions of extremal field.

The impossibility of a description, in terms of monoclinic spin Hamiltonian with $S = 1$, of the lines originated by copper complexes in TGFb: Cu^{2+} follows; this suggests that these lines have to be assigned to complexes consisting of more than two ions.

The strictly mathematical theory of spin Hamiltonian, and its derivation for the case under investigation, is given in Appendix.

1. Introduction

The angular dependence of resonance field in electron paramagnetic resonance exhibits certain low symmetry effects, such as non-coincidence of the axes of extremal resonance field values for various transitions and angular asymmetry with regard to these axes, which do not occur in the well known cases of axial and rhombic symmetry [1], [2]. Our aim is to provide a theoretical explanation, on the basis of an effective monoclinic spin Hamiltonian, of the possibility of these and similar effects for the case of $S = 1$.

The problem is connected with the question of the occurrence of more than two distinct resonance field extrema within a 180° angular period in systems described by such a Hamil-

* Work partly supported by the Institute of Physics, Department of Radiospectroscopy, Polish Academy of Sciences, Poznań.

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tonian. The presence of more than two such extrema was clearly observed for TGFB:Cu²⁺ by Stankowski [3] and the possibility of a description in terms of the discussed Hamiltonian would allow to assign the observed lines to the three energy levels of exchange-coupled pairs of copper ions (each single ion spin equal to 1/2). The monoclinic or even lower symmetry of these pairwise systems follows from the one-ion EPR spectrum and from structural investigations [4].

2. Spin Hamiltonian

Group-theoretical considerations similar to those of Grant and Strandberg [5] and Hauser [6] (expounded in a mathematically strict formulaion in Appendix) admit of the following form of spin Hamiltonian for the three states, well separated energetically from others, of the quantum-mechanical system in a monoclinic electrostatic field and uniform magnetic field \mathbf{H} :

$$\begin{aligned} \tilde{\mathcal{H}} = & D'S_{\zeta}^2 + E'(S_{\xi}^2 - S_{\eta}^2) + F'(S_{\xi}S_{\eta} + S_{\eta}S_{\xi}) + \\ & + \mu_B [g'_{\zeta\zeta}H_{\zeta}S_{\zeta} + (g'_{\xi\xi}H_{\xi} + g'_{\eta\xi}H_{\eta})S_{\xi} + (g'_{\xi\eta}H_{\xi} + g'_{\eta\eta}H_{\eta})S_{\eta}]. \end{aligned} \quad (1)$$

The ζ -direction is taken along the symmetry axis (the line of two-fold symmetry, or the line perpendicular to the mirror plane); the mutually perpendicular ξ and η axes (perpendicular to ζ) are taken arbitrarily. The g -tensor need not be symmetrical; however, its skew-symmetrical part is presumably very small (in the one-ion model of Abragam and Pryce [7] it is exactly equal to zero; for the two-ion model, when the Dzyaloshinsky-Moriya interactions exist, it is of the order of one per cent [8]), and so we will neglect it.

Henceforth, since the symmetry group defines no particular axes in the $\xi\eta$ -plane, we introduce a new coordinate system xyz , coinciding with the principal axes of the approximately symmetrical g -tensor (z -axis the same as the ζ -axis). The thus approximated Hamiltonian (1), in the new coordinate system, takes the form:

$$\begin{aligned} \tilde{\mathcal{H}} = & DS_z^2 + E(S_x^2 - S_y^2) + F(S_xS_y + S_yS_x) + \\ & + \mu_B (g_xH_xS_x + g_yH_yS_y + g_zH_zS_z). \end{aligned} \quad (2)$$

Let us observe that, because of symmetry non-equivalence of the z -axis and the x - and y -axes, we can make no *a priori* assumptions about the constants D and E (such as the relation $D > 3E$ for the rhombic case, where all the three mutually perpendicular axes are of two-fold symmetry and that of maximal anisotropy of the EPR spectrum can be chosen as z -axis).

The occurrence of the F -term entails a rotation of the system of principal axes of the "crystal field tensor" by an angle α ($\operatorname{tg} 2\alpha = F/E$) about the z -axis as compared to those of the g -tensor. In the case of a single ion with no orbitally degenerate crystal ground term, this difference in orientation of the two systems is due to spin-spin coupling (Abragam and Pryce [7], Roytsin [9]). For the case of $S = 1$, as far as we know, no such differences have been observed, maybe because of the smallness of the effect (monoclinic local symmetry is usually related with far distant coordination zones of surrounding ions). For the case of

pairs of ions (coupled to one another against the background of surrounding diamagnetic ions constituting a monoclinic crystal field), yet another mechanism connected with different possible orientations of the interaction axis with regard to the axes of the one-ion g -tensor and those of the crystal field tensor (Kurzyński [8]) permits the prediction of a large F -term, in contradistinction to the one-ion case.

Since the analytical Cardano solutions of the secular equation for the Hamiltonian (2) are quite useless for their complexity, we will discuss the problem, without numerical methods, in the two opposite approximations of a strong and weak magnetic field.

3. Strong magnetic field

The idea we shall apply was given, in another mathematical language, by Sachs [10]. For further calculations, it is convenient to express the crystal field part of the Hamiltonian (2) in terms of irreducible spherical tensor operators $P_m^l(\mathbf{S})$ (see Appendix):

$$\begin{aligned} \tilde{\mathcal{H}}_{\text{cr}} + \frac{2}{3}DP_0^0(\mathbf{S}) - \sqrt{\frac{2}{3}}DP_0^2(\mathbf{S}) - \\ - E(P_2^2(\mathbf{S}) + P_{-2}^2(\mathbf{S})) + iF(P_2^2(\mathbf{S}) - P_{-2}^2(\mathbf{S})). \end{aligned} \quad (3)$$

The reduced matrix element of operators $P^2(\mathbf{S})$, in the basis of eigenstates of the operator S_z , is:

$$\langle 1 || P^2(\mathbf{S}) || 1 \rangle = -\sqrt{\frac{2}{3}}. \quad (4)$$

For a strong magnetic field, the quantization axis lies approximately in the direction of the magnetic moment which, because of the anisotropy of the g -factor, can differ from the direction of the external magnetic field. Taking:

$$\begin{aligned} g_x H_x &= g_x H \sin \vartheta_0 \cos \varphi_0 =: gH \sin \vartheta \cos \varphi, \\ g_y H_y &= g_y H \sin \vartheta_0 \sin \varphi_0 =: gH \sin \vartheta \sin \varphi, \\ g_z H_z &= g_z H \cos \vartheta_0 =: gH \cos \vartheta, \end{aligned} \quad (5)$$

where ϑ_0, φ_0 define the direction of the magnetic field and ϑ, φ that of the magnetic moment referred to the principal axes x, y, z of the g -tensor (*cf.* Fig. 1), and:

$$\begin{aligned} g^2 &= g^2(\vartheta, \varphi) = g_x^2 \sin^2 \vartheta_0 \cos^2 \varphi_0 + g_y^2 \sin^2 \vartheta_0 \sin^2 \varphi_0 + g_z^2 \cos^2 \vartheta_0, \\ \cos \vartheta &= \frac{g_z}{g} \cos \vartheta_0, \\ \text{tg } \varphi &= \frac{g_y}{g_x} \text{tg } \varphi_0, \end{aligned} \quad (6)$$

we write the Zeemann part of the Hamiltonian (2) as:

$$\tilde{\mathcal{H}}_{\text{mg}} = \mu_B g H S'_z, \quad (7)$$

where

$$S'_z = S_x \sin \vartheta \cos \varphi + S_y \sin \vartheta \sin \varphi + S_z \cos \vartheta \quad (8)$$

is the spin operator component along the magnetic moment direction, chosen as z' -axis.

We now proceed to express the irreducible spherical tensor operators in the new coordinate system in accordance with the defining formula:

$$P_n^2(\mathbf{S}) = \sum_{m=-2}^2 D^{(2)}(\{0\vartheta\varphi\})_{mn} P_m^2(\mathbf{S}'), \quad (9)$$

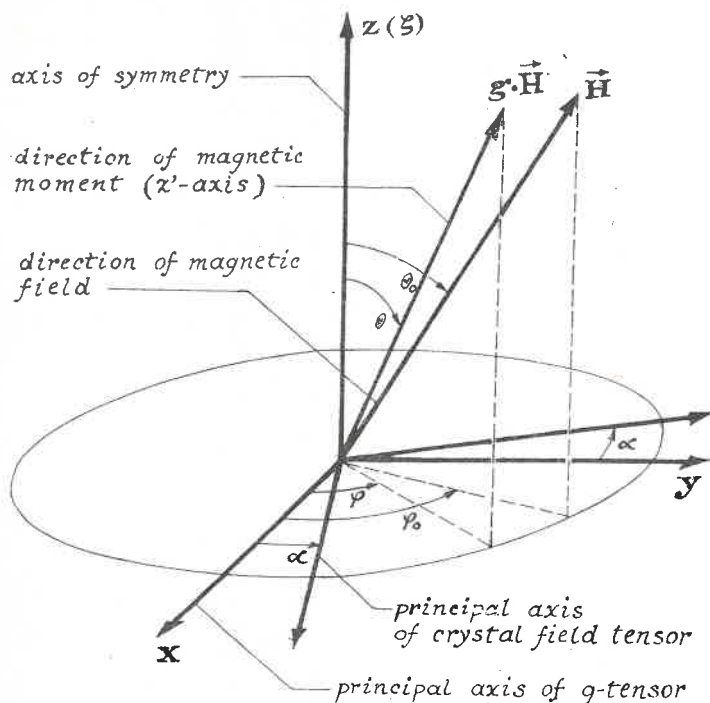


Fig. 1

where

$$D^{(2)}(\{0\vartheta\varphi\})_{mn} = d_{mn}^{(2)}(\vartheta) e^{in\varphi} \quad (10)$$

($\{0\vartheta\varphi\}$ denotes the Euler angles of rotation of the coordinate system); whence the whole Hamiltonian (2) in the new coordinate system $x' y' z'$ attached to the magnetic moment is:

$$\begin{aligned} \tilde{\mathcal{H}} = & \mu_B g H S'_z + \frac{2}{3} D P_0^2(\mathbf{S}') - \sum_{m=-2}^2 \left[\frac{\sqrt{2}}{3} D d_{m0}^{(2)}(\vartheta) + \right. \\ & \left. + (E - iF) e^{2i\varphi} d_{m2}^{(2)}(\vartheta) + (E + iF) e^{-2i\varphi} d_{m-2}^{(2)}(\vartheta) \right] P_m^2(\mathbf{S}'). \end{aligned} \quad (11)$$

Resorting to the Wigner-Eckart theorem, and with regard to (4), the matrix elements of (11) in the basis of eigenstates of S'_z are:

$$\begin{aligned} \langle M' | \tilde{\mathcal{H}} | N' \rangle = & (\mu_B g H M' + \frac{2}{3} D) \delta_{M'N'} + \sqrt{\frac{5}{2}} \langle 2, M' - N', 1, N' | 2, 1, 1, M' \rangle \times \\ & \times \left[\frac{\sqrt{2}}{3} D d_{M'-N',0}^{(2)}(\vartheta) + (E - iF) e^{2i\varphi} d_{M'-N',2}^{(2)}(\vartheta) + (E + iF) e^{-2i\varphi} d_{M'-N',-2}^{(2)}(\vartheta) \right]. \end{aligned} \quad (12)$$

Denoting:

$$E_0 = +\sqrt{E^2+F^2}, \quad \operatorname{tg} 2\alpha = \frac{F}{E},$$

$$U = D - E_0 \cos 2(\varphi - \alpha), \quad V = E_0 \sin 2(\varphi - \alpha) \quad (13)$$

and taking the explicit form of the Wigner functions $d_{mn}^{(2)}$, we may write this matrix as given in Table I.

TABLE I

Matrix of Hamiltonian $\tilde{\mathcal{H}}$ in the basis of eigenstates of S_z' (component of spin vector operator in the direction of magnetic moment)

	$ -1\rangle$	$ 0\rangle$	$ 1\rangle$
$\langle -1 $	$-\mu_B g H + D - \frac{1}{2} U \sin^2 \vartheta$	$\frac{\sin \vartheta}{\sqrt{2}} (U \cos \vartheta + iV)$	$V + \frac{1}{2} U \sin^2 \vartheta - iV \cos \vartheta$
$\langle 0 $	$\frac{\sin \vartheta}{\sqrt{2}} (U \cos \vartheta - iV)$	$U \sin^2 \vartheta$	$-\frac{\sin \vartheta}{\sqrt{2}} (U \cos \vartheta + iV)$
$\langle 1 $	$V + \frac{1}{2} U \sin^2 \vartheta + iV \cos \vartheta$	$-\frac{\sin \vartheta}{\sqrt{2}} (U \cos \vartheta - iV)$	$\mu_B g H + D - \frac{1}{2} U \sin^2 \vartheta$

In the second order of perturbation calculus for the strong magnetic field case¹, i.e. for

$$\mu_B g H \gg D, E, F, \quad (14)$$

we obtain from this matrix the following approximate eigenvalues of the Hamiltonian (2):

$$W_{\pm 1}^{(2)} = \pm \mu_B g H + D - \frac{1}{2} U \sin^2 \vartheta \pm$$

$$\pm \frac{1}{2\mu_B g H} \left[U^2 \sin^2 \vartheta \left(\cos^2 \vartheta + \frac{1}{4} \sin^2 \vartheta \right) + UV \sin^2 \vartheta + 2V^2 \right]$$

$$W_0^{(2)} = U \sin^2 \vartheta. \quad (15)$$

The selection rules in a high frequency magnetic field perpendicular to the constant field allows, for this case, the transitions $1 \rightarrow 0$ and $0 \rightarrow -1$:

$$W_1(H_{r+}) - W_0(H_{r+}) = h\nu$$

$$W_0(H_{r-}) - W_{-1}(H_{r-}) = h\nu. \quad (16)$$

¹ This of course, does not mean that the magnetic field is larger in energy than the electric (crystal) field but, e. g. in the model of Abragam and Pryce, that the effect of the magnetic field on the spin is stronger than that of the crystal field *via* the spin-orbit coupling.

From (15), we derive the following angular dependence of the corresponding resonance magnetic field:

$$H_{r\pm} = \frac{1}{2\mu_B g} \left\{ h\nu \mp \left(D - \frac{3}{2} U \sin^2 \vartheta \right) + \left[\left(h\nu \mp \left(D - \frac{3}{2} U \sin^2 \vartheta \right) \right)^2 - 2 \left(U^2 \sin^2 \vartheta \left(\cos^2 \vartheta + \frac{1}{4} \sin^2 \vartheta \right) + UV \sin^2 \vartheta + 2V^2 \right) \right]^{1/2} \right\} \quad (17)$$

or, expanding the square root with regard to the smallness of the second order correction:

$$H_{r\pm} = \frac{1}{\mu_B g} \left\{ h\nu \pm \left(D - \frac{3}{2} U \sin^2 \vartheta \right) - \frac{U^2 \sin^2 \vartheta \left(\cos^2 \vartheta + \frac{1}{4} \sin^2 \vartheta \right) + UV \sin^2 \vartheta + 2V^2}{h\nu \mp \left(D - \frac{3}{2} U \sin^2 \vartheta \right)} + \dots \right\} \quad (18)$$

The first term in the above formula corresponds to the zeroth order of perturbation calculus, the second — to the first order, whereas the third and the higher terms, proportional to higher powers of trigonometrical functions (which we neglect) are due to the second order of perturbation calculus.

4. Weak magnetic field

The matrix of the Hamiltonian (2) in the basis of eigenstates of the operator S_z $\{|-1\rangle, |0\rangle, |1\rangle\}$ (in the system of principal axes of the g -tensor), is given in Table II.

TABLE II

Matrix of Hamiltonian $\tilde{\mathcal{H}}$ in the basis of eigenstates of S_z (component of spin vector operator in the direction of twofold-symmetry axis)

	$ -1\rangle$	$ 0\rangle$	$ 1\rangle$
$\langle -1 $	$D - \mu_B g_z H_z$	$\frac{\eta_B}{\sqrt{2}} (g_x H_x + i g_y H_y)$	$E + iF$
$\langle 0 $	$\frac{\mu_B}{\sqrt{2}} (g_x H_x - i g_y H_y)$	0	$\frac{\mu_B}{\sqrt{2}} (g_x H_x + i g_y H_y)$
$\langle 1 $	$E - iF$	$\frac{\mu_B}{\sqrt{2}} (g_x H_x - i g_y H_y)$	$D + \mu_B g_z H_z$

At zero magnetic field, the energy values are:

$$W_a = D + E_0, \quad W_b = D - E_0, \quad W_c = 0 \quad (19)$$

and the corresponding eigenstates of the crystal-field part of this Hamiltonian become:

$$\begin{aligned} |a\rangle &= \frac{1}{\sqrt{2}}|-1\rangle + \frac{E-iF}{\sqrt{2}E_0}|1\rangle, \\ |b\rangle &= -\frac{E+iF}{\sqrt{2}E_0}|-1\rangle + \frac{1}{\sqrt{2}}|1\rangle, \\ |c\rangle &= |0\rangle. \end{aligned} \quad (20)$$

The matrix elements of the whole Hamiltonian (2) taken in the basis $\{|a\rangle, |b\rangle, |c\rangle\}$ of eigenstates of the crystal field Hamiltonian considered as unperturbed in the case under discussion here, are:

$$\begin{aligned} \langle a|\tilde{\mathcal{H}}|a\rangle &= D+E_0, \\ \langle b|\tilde{\mathcal{H}}|b\rangle &= D-E_0, \\ \langle c|\tilde{\mathcal{H}}|c\rangle &= 0, \\ \langle a|\tilde{\mathcal{H}}|b\rangle &= \frac{\mu_B}{E_0}(E+iF)g_zH_z, \\ \langle b|\tilde{\mathcal{H}}|c\rangle &= \frac{\mu_B}{2E_0}\{(E_0-E)g_xH_x-Fg_yH_y\}+i[Fg_xH_x-(E_0+E)g_yH_y] \\ \langle c|\tilde{\mathcal{H}}|a\rangle &= \frac{\mu_B}{2E_0}\{(E_0+E)g_xH_x+Fg_yH_y\}-i[Fg_xH_x+(E_0-E)g_yH_y]. \end{aligned} \quad (21)$$

The first order of perturbation procedure, for E_0 of the order of $\frac{1}{3}D$, contributes no correction to the zero-field energies; in the second order, we obtain:

$$\begin{aligned} W_a^{(2)} &= D+E_0 + \frac{\mu_B^2 g^2}{2E_0} \left(1 - \frac{U \sin^2 \vartheta}{D+E_0}\right) H^2, \\ W_b^{(2)} &= D-E_0 - \frac{\mu_B^2 g^2}{2E_0} \left(1 - \frac{U \sin^2 \vartheta}{D-E_0}\right) H^2, \\ W_c^{(2)} &= -\frac{\mu_B^2 g^2 U \sin^2 \vartheta}{(D-E_0)(D+E_0)} H^2. \end{aligned} \quad (22)$$

From (21) it follows that there are, in general, three permitted transitions in the perpendicular high-frequency field. The corresponding resonance fields are:

$$\begin{aligned} H_r(a \rightarrow c) &= \frac{1}{\mu_B g} \sqrt{\frac{2(h\nu - D - E_0) E_0 (D + E_0) (D - E_0)}{D^2 - E_0^2 + (3E_0 - D) U \sin^2 \vartheta}}, \\ H_r(b \rightarrow c) &= \frac{1}{\mu_B g} \sqrt{\frac{2(h\nu - D + E_0) E_0 (D + E_0) (D - E_0)}{-D^2 + E_0^2 + (3E_0 + D) U \sin^2 \vartheta}}, \\ H_r(a \rightarrow b) &= \frac{1}{\mu_B g} \sqrt{\frac{(h\nu - 2E_0) E_0 (D + E_0) (D - E_0)}{D^2 - E_0^2 - DU \sin^2 \vartheta}}. \end{aligned} \quad (23)$$

5. Discussion

By replacing the angles ϑ_0, φ_0 by angles ϑ, φ , we were able to separate the influence of g -factor anisotropy from pure crystal-field tensor effects in the angular dependence of the resonance field, as expressed by formulas (18) and (23).

The contribution from the g -tensor is found, from Eqs (6), to be of the form:

$$g^2(\vartheta, \varphi) = (g_x^{-2} \sin^2 \vartheta \cos^2 \varphi + g_y^{-2} \sin^2 \vartheta \cos^2 \varphi + g_z^{-2} \cos^2 \vartheta)^{-1}. \quad (24)$$

The extrema of this expression are the following:

$$\vartheta = 0; \quad \vartheta = \frac{\pi}{2}, \quad \varphi = 0; \quad \vartheta = \frac{\pi}{2}, \quad \varphi = \frac{\pi}{2}. \quad (25)$$

The main term describing the crystal field tensor effects in the resonance magnetic field anisotropy (due to the first order of perturbation procedure for the strong field (18), and to the second order for a weak field (23)), is:

$$U \sin^2 \vartheta = (D - E_0 \cos 2(\varphi - \alpha)) \sin^2 \vartheta. \quad (26)$$

There exist three extrema of this expression:

$$\vartheta = 0; \quad \vartheta = \frac{\pi}{2}, \quad \varphi = \alpha; \quad \vartheta = \frac{\pi}{2}, \quad \varphi = \alpha + \frac{\pi}{2}. \quad (27)$$

The values (25) and (27) are seen to differ in the xy -plane by an angle α . Hence, the resultant angles for extremal values of the resonance field lie in the angular intervals $0 \leq \varphi \leq \alpha$ and $\frac{\pi}{2} \leq \varphi \leq \frac{\pi}{2} + \alpha$; the angles for these extrema follow the relation of the anisotropies of the expressions (24) and (26), and depend strongly on the magnitude of the magnetic field. The angles are not the same for the various transitions. It follows from (18) and (23) that there exist in general more than single extrema inside the above intervals; their difference in magnitude is however small, in any case less than the corresponding g -factor anisotropy.

For the angles given in (27), the secular equation of the Hamiltonian (2):

$$W^3 - 2DW^2 + (D^2 - E_0^2 - g^2 \mu_B^2 H^2)W + U \sin^2 \vartheta g^2 \mu_B^2 H^2 = 0 \quad (28)$$

possesses one field-independent solution, and the corresponding eigenvalues are easily found:

for $\vartheta = 0$:

$$\begin{aligned} W_a &= D + \sqrt{E_0^2 + g_z^2 \mu_B^2 H^2}, \\ W_b &= D - \sqrt{E_0^2 + g_z^2 \mu_B^2 H^2}, \\ W_c &= 0, \end{aligned} \quad (29a)$$

for $\vartheta = \frac{\pi}{2}$, $\varphi = \alpha$:

$$\begin{aligned}
 W_a &= \frac{D+E_0}{2} + \sqrt{\left(\frac{D+E_0}{2}\right)^2 + g^2 \left(\frac{\pi}{2}, \alpha\right) \mu_B^2 H^2}, \\
 W_b &= D - E_0, \\
 W_c &= \frac{D+E_0}{2} - \sqrt{\left(\frac{D+E_0}{2}\right)^2 + g^2 \left(\frac{\pi}{2}, \alpha\right) \mu_B^2 H^2},
 \end{aligned} \tag{29b}$$

for $\vartheta = \frac{\pi}{2}$, $\varphi = \alpha + \frac{\pi}{2}$:

$$\begin{aligned}
 W_a &= D + E_0, \\
 W_b &= \frac{D-E_0}{2} + \sqrt{\left(\frac{D-E_0}{2}\right)^2 + g^2 \left(\frac{\pi}{2}, \alpha + \frac{\pi}{2}\right) \mu_B^2 H^2}, \\
 W_c &= \frac{D-E_0}{2} - \sqrt{\left(\frac{D-E_0}{2}\right)^2 + g^2 \left(\frac{\pi}{2}, \alpha + \frac{\pi}{2}\right) \mu_B^2 H^2}.
 \end{aligned} \tag{29c}$$

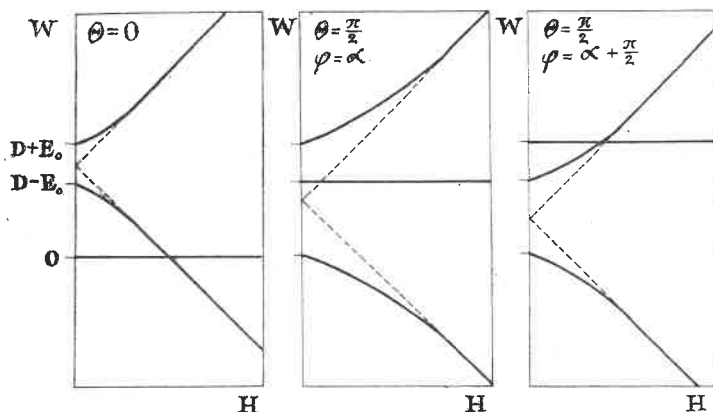


Fig. 2

A diagram of the splitting in function of the magnetic field is given in Fig. 2; as is seen, it is the same as for the rhombic case, with E_0 substituted by E .

The crystal field tensor effects are usually larger than those of g -factor anisotropy. It follows from the preceding remarks that the Zeeman splitting in the directions of the extremal resonance magnetic field (but not the angular dependence) can be described approximately in terms of the rhombic Hamiltonian.

The resonance field, as one can see from (28) and (6), is exactly symmetrical with respect to $\vartheta_0 = 0$ and $\vartheta_0 = \frac{\pi}{2}$, but it follows from (6) that for $g_x \neq g_y$

$$\operatorname{tg} \alpha_0 \neq -\operatorname{ctg} \left(\alpha + \frac{\pi}{2} \right)_0 \quad \text{and} \quad \cos 2(\varphi - \alpha)_0 \neq -\cos 2(-\varphi + \alpha)_0.$$

so that, assuming the angles of extremal values of the resonance field as those given by (27), we can expect a departure from an angle of $\frac{\pi}{2}$ between the directions of the extremal field in the xy -plane, as well as a large angular asymmetry with regard to these axes.

The second order of perturbation procedure for a strong magnetic field leads to further corrections in the angular dependence of the resonance field, such as additional extrema, but, as one easily sees on putting $E_0 = E$ and $\alpha = 0$ in (18), these corrections are the same as for the cases of rhombic and even higher symmetry (see for this problem the monograph of Low [11]). The neglected asymmetry properties of the g -tensor may cause slight deviations from 180° -symmetry in the spectrum.

The all cases of the small denominators going to zero in the second order corrections in (18) and (23) are connected with the strong angular dependence of the transition probabilities similar to the higher symmetry cases, and we will not discuss them here.

From the preceding considerations it follows that it is not possible to explain, on the basis of a monoclinic spin Hamiltonian, the anomalous behaviour of the observed angular dependence of the resonance field for TGFBCu²⁺ [3], because the deviations from the approximate shape (18) are much larger than the admissible influence of g -factor anisotropy. This, in conjunction with the impossibility of a description by way of a rhombic Hamiltonian in the directions of the extremal resonance field values [12] suggests that the observed lines belong to a spin larger than 1, attributable to complexes with more than two copper ions.

APPENDIX A

Let us consider the n -dimensional unitary space L of states of a quantum-mechanical system with point symmetry described by the group G , and let \mathcal{H} be the Hamiltonian of the system. There exist, by definition, a representation T of G in L , not necessarily irreducible, for which the relation

$$[\mathcal{H}, T(g)] = 0 \quad (\text{A1})$$

holds for every $g \in G$.

Now let L_S be the $2S+1 = n$ -dimensional space of the representation $D^{(S\pm)}$ of the full orthogonal group $O(3)$. We can deal with the elements of L_S (transforming by rotations like spherical harmonics) as eigenstates of the z -component of the angular momentum operator S .

Let σ be a one-to-one mapping of L onto L_S such that for every $\psi, \varphi \in L$, and for every $g \in G$:

$$\langle \psi | \varphi \rangle = \langle \sigma\psi | \sigma\varphi \rangle \quad (\text{unitarity}) \quad (\text{A2a})$$

$$D^{(S\pm)}(g)\sigma\psi = \sigma T(g)\psi \quad (\text{conservation of transformational properties}). \quad (\text{A2b})$$

Such a mapping exists if and only if T and $D^{(S\pm)}$ are unitarily equivalent representations of the group $G \subset O(3)$, but in general is not unique.

L is by definition an invariant subspace of the Hamiltonian \mathcal{H} and we may define the σ -picture $\tilde{\mathcal{H}}$ of the limitation of \mathcal{H} to L , which possesses the following properties:

$$\langle \sigma\psi | \tilde{\mathcal{H}} | \sigma\varphi \rangle = \langle \psi | \mathcal{H} | \varphi \rangle, \text{ for every } \psi, \varphi \in L, \quad (\text{A3a})$$

$$[\tilde{\mathcal{H}}, D^{(S\pm)}(g)] = 0, \text{ for every } g \in G. \quad (\text{A3b})$$

If a mapping σ exists, $\tilde{\mathcal{H}}$ exists and is, from quantum-mechanical point of view, an exact effective Hamiltonian for the manifold of states spanning L , and will be referred to as the spin Hamiltonian for this manifold.

Linear operators in L_S form a linear space isomorphic to $L_S \otimes L_S^*$; in this space, the product representation $D^{(S\pm)} \otimes D^{(S\pm)*}$ of orthogonal group is induced. The Clebsch-Gordan decomposition

$$D^{(S\pm)} \otimes D^{(S\pm)*} = \bigoplus_{l=0}^{2S} D^{(l+)} \quad (\text{A4})$$

of this representation is realized in the basis of irreducible spherical tensor operators transforming according to even irreducible representations of the orthogonal group:

$$D^{(S\pm)}(R) P_n^l D^{(S\pm)}(R) = \sum_{m=-l}^l D^{(l+)}(R)_{mn} P_m^l, \text{ for every } R \in O(3). \quad (\text{A5})$$

The effective Hamiltonian can hence be given in the form of a linear combination of irreducible spherical tensor operators P_m^l with integer $l \leq 2S$, and even with respect to space inversion. By (A3b), such a combination has to be the same as the one which decomposes the reducible representations $D^{(l+)}$ of group G into irreducible identity representations T_1 .

Such combinations are given *e.g.* in [13] and, for the case of $S=1$ and monoclinic symmetry ($G = C_{2h}, C_2, C_s$) we obtain:

$$\begin{aligned} \tilde{\mathcal{H}} = & b_0^0 P_0^0 + i b_0^1 P_0^1 + b_0^2 P_0^2 + \\ & + \frac{1}{\sqrt{2}} b_2^3 (P_2^3 + P_{-2}^3) + \frac{i}{\sqrt{2}} b_{-2}^2 (P_2^2 - P_{-2}^2). \end{aligned} \quad (\text{A6})$$

Here, we have taken into account the hermicity of the Hamiltonian, assuming the normalizing factors to satisfy the relation:

$$(P_m^l)^* = (-1)^{l-m} P_{-m}^l \quad (\text{A7})$$

and the phenomenological constants b_m^l as real.

Let us note that the spin Hamiltonian is, according to (A5), invariant under space inversion, also in the case of a group G containing no such element. This is due to the circumstance that the effective Hamiltonian can in general possess higher symmetry than the "real" one.

It is convenient to express the irreducible spherical tensor operators in the form $P_m^l(\mathbf{S})$ of homogeneous polynomials of degree l in components of the angular momentum operator \mathbf{S} (Koster and Staatz [14]). Because of antisymmetry of the operator \mathbf{S} with respect to time

reversal, the $P_m^l(\mathbf{S})$'s with even l have to describe the behaviour of the system in an external electric field (*e.g.* crystal field), in contradistinction to those with odd l , which describe an external magnetic field. The term with $l = 0$ leads to an additive constant in the energy, which we can take arbitrarily.

According to the above remark, the crystal field spin Hamiltonian for our case has to be of the form:

$$\begin{aligned} \tilde{\mathcal{H}}_{\text{cr}} = & \frac{2}{3} DP_0^0(\mathbf{S}) - \sqrt{\frac{2}{3}} DP_0^2(\mathbf{S}) - \\ & - E(P_2^2(\mathbf{S}) + P_{-2}^2(\mathbf{S})) + iF(P_2^2(\mathbf{S}) - P_{-2}^2(\mathbf{S})) \end{aligned} \quad (\text{A8})$$

where, in the normalizing convention (A7):

$$\begin{aligned} P_0^0(\mathbf{S}) &= 1 \\ P_0^2(\mathbf{S}) &= -\frac{3}{\sqrt{6}} \left(S_\xi^2 - \frac{1}{3} S(S+S) \right) \\ P_{\pm}^2(\mathbf{S}) &= -\frac{1}{2} S_{\pm}^2 = -\frac{1}{2} (S_\xi \pm iS_\eta)^2. \end{aligned} \quad (\text{A9})$$

The $\xi\eta\zeta$ coordinate system is attached to the crystal field, with ξ and η taken arbitrarily and ζ -axis taken along the symmetry axis. We have introduced the usual crystal field parameters as phenomenological constants.

For the case of interest here, the magnetic field is much less (by two orders of magnitude at least) than the electric crystal field, so we can assume, in a good approximation, that it does not destroy the monoclinic symmetry of the system. The Zeemann part of the Hamiltonian has to be contravariant under simultaneous rotations of the magnetic and electric ($\xi\eta\zeta$ system of axes) fields, so that in the approximation assumed, it has to contain the following terms:

$$\begin{aligned} P_0^l(\mathbf{S}, \mathbf{H}) &= \sum_{m=-1,0,1} \langle 1, m, 1, -m | 1, 1, l, 0 \rangle P_m^l(\mathbf{H}) P_{-m}^1(\mathbf{S}); \quad l = 0, 1, 2, \\ P_{\pm}^2(\mathbf{S}, \mathbf{H}) &= \sum_{m=-1,0,1} \langle 1, m, 1, -m \pm 2 | 1, 1, 2, \pm 2 \rangle P_m^1(\mathbf{H}) P_{-m}^1(\mathbf{S}). \end{aligned} \quad (\text{A10})$$

We have neglected powers of \mathbf{H} higher than linear. Substituting the appropriate Clebsch-Gordan coefficients and taking $P_m^1(\mathbf{H})$ and $P_m^1(\mathbf{S})$ from Ref. [14] (formally, we have to multiply operators of Koster and Staats by factors i^l in order that the condition (A7) shall be satisfied), we obtain the Zeeman spin Hamiltonian for the monoclinic system with $S = 1$ in the form:

$$\begin{aligned} \tilde{\mathcal{H}}_{\text{mgt}} = & \mu_B [g'_{\zeta\zeta} H_\zeta S_\zeta + (g'_{\xi\xi} H_\xi + q'_{\eta\xi} H_\eta) S_\xi + \\ & + (g'_{\xi\eta} H_\xi + g'_{\eta\eta} H_\eta) S_\eta]. \end{aligned} \quad (\text{A11})$$

We have introduced the usual g -tensor in place of the five phenomenological constants occurring in (A6). Let us observe that, because of P_0^1 in (A6), $g'_{\xi\eta}$ differs in general from $g'_{\eta\xi}$.

For the particular theory of effective operators, see *e.g.* the monograph by Judd [15].

The author wishes to thank Docent dr hab. L. Kowalewski for discussing the manuscript in detail and for his interest throughout this investigation. The author would also like to thank Docent dr hab. J. Stankowski and M. Maćkowiak, M. Sci., for suggesting the topics and for their interesting discussions.

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